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INVESTIGATION OF CATALYTIC REDUCTION AND FILTER TECHNIQUES FOR SIMULTANEOUS MEASUREMENTS OF NO, NO₂ AND HNO₃ IN THE STRATOSPHERE

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ABSTRACT

A concept for measuring stratospheric NO_y-species is presented which utilizes the catalytic reduction of NO₂ and HNO₃ over heated metal catalysts and the chemisorption of HNO₃ on Nylon.

Using the MPAE chemiluminescent balloon-borne sonde, stratospheric NO and NO₂ profiles have been measured since 1983. NO is detected by chemiluminescence produced in reaction with O₃ while NO₂ needs first to be converted to NO over a heated stainless steel catalyst.

To improve this technique for simultaneously measuring HNO₃, the catalytic reduction of NO₂ and HNO₃ over several metal catalysts and the chemisorption of NO₂ and HNO₃ on Nylon have been investigated in laboratory tests. The results of these tests under simulated stratospheric conditions are presented in detail in this paper. They demonstrate that the simultaneous measurement of NO, NO₂ and HNO₃ is indeed possible with the combination of stainless steel or Au as a catalyst and a nylon filter.

1. INTRODUCTION

The oxides of nitrogen (NO and NO₂) and nitric acid (HNO₃) play an important role in the chemistry of the stratosphere where they are involved in photochemical reaction cycles that produce or destroy ozone.

A balloon borne sonde was developed at the Max-Planck-Institut für Aeronomie and flown first in 1977 to measure vertical profiles of nitrogen oxide (NO) in the stratosphere. The measurement is based on the chemiluminescence principle given by Clyne et al. [1964], Clough and Trush [1967] and Fontijn et al. [1970] who utilized the gas reaction between NO and O₃ in which a determined percentage of activated NO₂ is formed.

With a modified balloon sonde, NO and NO+NO₂ were measured in turn during the 1983 MAP/GLOBUS campaign. From these measurements daytime NO and NO₂ profiles were determined [Fabian et al., 1987; Pommereau et al., 1987]. The measurement of NO+NO₂ was made possible by leading the air over a stainless steel catalyst which

converts NO₂ to NO. This paper describes the laboratory investigations carried out on several catalysts and on Nylonwool. The scope was to measure NO, NO₂ and HNO₃ simultaneously with the sonde in the stratosphere.

2. EXPERIMENTAL

A schematic diagram of the experimental setup for testing various catalysts is shown in Fig. 1.

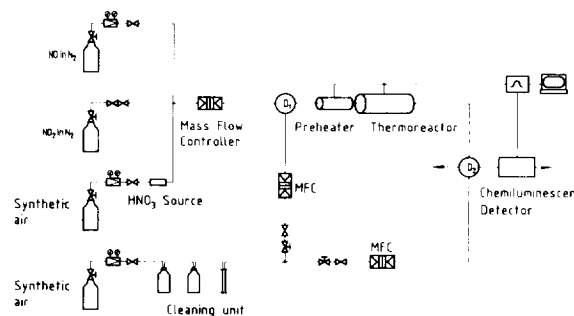


Fig. 1. Schematic diagram of the experimental setup for testing the catalysts.

Synthetic air which was further purified by silicagel, active coal and molecular sieve was used as carrier gas. The calibration gases (1 ppm NO in N₂ and 10 ppm NO₂ in N₂) contained in aluminium cylinders and HNO₃ in synthetic air were added to the carrier gas in the dilution unit D₁.

The HNO₃ calibration mixture was provided by a permeation source based on the principle given by Flocke et al. [1988] (Fig. 2). A flow of 2 ml/min synthetic air was pumped through a teflon tube which was immersed in a glass containing 2 parts of HNO₃ and 1 part of H₂SO₄. Calibration of the source with an ion chromatograph showed that it is impossible to get a flow which contains only HNO₃. In spite of H₂SO₄, NO₂ also permeated through the teflon tube. The proportion of the concentrations c_{NO₂} : c_{HNO₃} was around 4:6. To yield stable permeation rates of around 5 ppm, the temperature of the source was

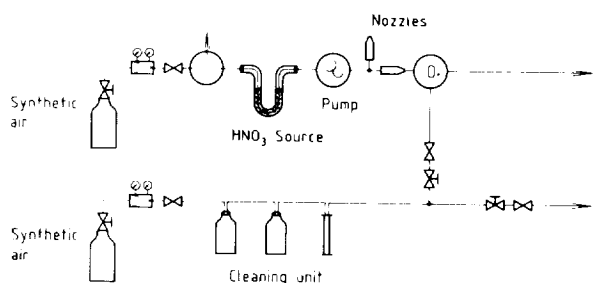


Fig. 2. Schematic diagram of the HNO₃ permeation unit.

held constant at 0°C. Furthermore, a pump was placed downstream the glass and an overflow upstream the glass. So, the source was not influenced by pressure changes in the other part of the experiment which would have caused large differences of the permeation rate. To yield mixing ratios of a few ppb of (NO₂ + HNO₃) the flow was splitted with two glass nozzles before reaching the dilution unit D₁.

After leaving the dilution unit the gas passed through two metal block ovens, a preheater and a thermoreactor which contained the respective catalyst. Two chemiluminescent detectors (model 8440, Monitor Labs and model LMA-3 of Scintrex/Unisearch) have been used to measure the products of the catalysis. In D₂ a flow of around 250 ml/min of synthetic air was added to the stream leaving the thermoreactor because the analysers needed flows of 500 ml/min or 1.5 l/min. The lowest mixing ratios reached with the presented setup are some tenth of a ppb for NO and NO₂ and a few ppb for NO₂+HNO₃. To vary the pressure, the thermoreactor was installed in the low-pressure part of the ML-analyser.

Au, Cu, Fe, Ni, NiCr, Mo and stainless steel (X 5 Cr Ni 189) catalysts have been chosen for the tests. Although the conversion qualities of most of these catalysts have been tested in other investigations (often under addition of CO) [e.g. Winer et al., 1974; Bollinger et al., 1983; Fahey et al., 1985], all the catalysts were tested again. These measurements were necessary, because structure differences, manufacturing faults and impurities can strongly influence the catalytic behaviour. All the catalysts except Au were high purity wires of the respective material with diameters from 1 mm to 1.3 mm. The Au catalyst consisted of a copper wire which was coated with a 5 μm gold layer. The coating consisted of so many atomic layers that this wire could be considered a pure Au catalyst. The diffusion of Cu to the surface could be observed at temperatures higher than 300°C only.

In practice every catalyst consisted of four inert glass tubes as catalyst carriers (Duran, length = 94 cm, i.e. = 0.3 cm, o.d. 0.6 cm) passing through the preheater and the thermoreactor. A length of 20 cm of each tube is filled with the respective catalyst wire in such a manner that the

middle of each filling was 4 cm behind the middle of the thermoreactor. This, in addition to the splitting of the gas stream through the four tubes, minimized the temperature differences within the fillings. The maximum temperature difference did not exceeded 3.4°C even at temperatures as high as 500°C.

3. RESULTS AND DISCUSSION

The possible conversion of NO and the conversion of NO₂ and HNO₃ to NO were studied first under normal pressure as a function of catalyst material and catalyst temperature up to 450°C. The flow over the catalyst was 250 ml/min.

NO mixing ratios from 0.9 to 85 ppb were found to be influenced by Ni and NiCr catalysts, whereas over Au, Cu, Fe, Mo and stainless steel catalysts no change of the mixing ratios occurred. Therefore, Ni and NiCr were excluded from further investigations. A complete conversion of NO₂ mixing ratios of 0.9–90 ppb and NO₂+HNO₃ mixing ratios of 4–50 ppb took place over the rest of the catalysts except Cu in the temperature domains listed in Table 1. The catalytic behaviour of Fe, stainless steel and Au are shown in Figures 3 and 4.

Table 1. Temperature domains ΔT_{NO₂} and ΔT_{NO₂+HNO₃} where complete conversions of NO₂ and NO₂ + HNO₃ to NO over the catalysts were observed.

catalyst	ΔT _{NO₂}	ΔT _{NO₂+HNO₃}
Mo	235°C – 450°C	285°C – 450°C
Fe	160°C – 300°C	265°C – 300°C
Au (on Cu)	120°C – 300°C	210°C – 300°C
Stainless steel	150°C – 450°C	180°C – 450°C

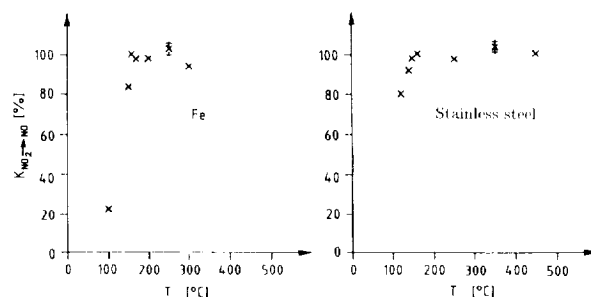
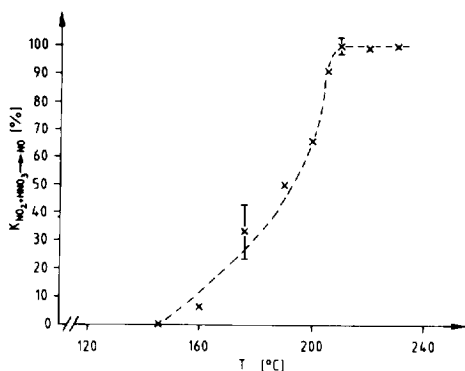


Fig. 3. Conversion of 93 ppb NO₂ in N₂ to NO as a function of temperature over Fe and stainless steel catalysts.

It is striking that there is e.g. no conversion of NO₂+HNO₃ to NO over Au at the temperature T = 135°C, whereas the conversion of NO₂ (without HNO₃) to NO is complete. It seems that the NO₂ conversion is influenced



Conversion of 5.1 ppb $\text{NO}_2 + \text{HNO}_3$ to NO as a function of temperature over an Au catalyst.

by the presence of HNO_3 . For all the catalysts tested no temperatures could be found where only a conversion of NO_2 to NO or HNO_3 to NO could be observed.

A complete conversion of NO_2 and HNO_3 was also observed over Au ($T=250^\circ\text{C}$) Fe, Mo and stainless steel ($T=300^\circ\text{C}$) at a pressure of 50 mbar. As pointed out by Fahey et al. [1985] Mo and FeSO_4 lose their catalytic activity under stratospheric O_3 concentrations. In our tests mixing ratios of 1–3 ppm O_3 caused a reduced activity of the Fe and Mo catalysts. The catalytic activity of Au and stainless steel catalysts were not influenced by these O_3 mixing ratios.

In addition, the four catalysts were observed with an electron microsonde. It turned out that Au and stainless steel catalysts were never oxidized, whereas Fe and Mo catalysts were always found to be oxidized after use. Mo and Fe catalysts which had been used for 96 h or longer always showed a complete oxidation and a reduced activity.

Since we only observed the conversion of $\text{NO}_2 + \text{HNO}_3$ to NO by the catalysts tested but never the conversion of NO_2 to NO or HNO_3 to NO alone, a nylon trap was constructed in order to remove the HNO_3 from the gas stream. Nylon has been used very often for this purpose under tropospheric conditions [e.g. Miller and Spicer, 1975; Joseph and Spicer, 1978; Huebert et al., 1990]. In our test a glass tube ($l = 60$ cm, i.d. = 12 mm) was filled with 10 g of Nylonwool. With this tube $93 \pm 5\%$ of the HNO_3 could be removed from the gas stream at a pressure of $p = 50$ mbar.

With this result it is possible in principle to build a three channel system to measure NO, NO_2 and HNO_3 simultaneously. NO is detected in the first channel by chemiluminescence produced in reaction with O_3 . In the second channel, NO_2 and HNO_3 are converted to NO over a heated stainless steel or Au catalyst, which enables determination of $\text{NO} + \text{NO}_2 + \text{HNO}_3$. In the third channel, a nylon trap which removes HNO_3 from the gas stream is combined with an Au or stainless steel catalyst thus allowing for measuring $\text{NO} + \text{NO}_2$. The single constituents can simply be determined by calculating the respective differences.

ACKNOWLEDGEMENT

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